1905

Analytical determination of copper products

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THESIS

FOR THE

Degree of Bachelor of Science

IN

Chemistry and Metallurgy.

SUBJECT:

"Analytical Determination of Copper Products."

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JUNE 9, 1905.

ANALYTICAL DETERMINATION OF COPPER PRODUCTS.

It is a well known fact that the presence of impuritie in copper products has been a source of annoyance to the Chemist. The object of this thesis was to make myself familiar with the actions of different impurities in copper products, and the methods for the determination of Arsenic in the same.

Owing to the fact that it has taken me longer than expected I have been unable to cover all the points that I first intended to.

I will first take up the subject of methods for the determination of Copper in copper ores.

ASSAY OF COPPER ORES.

1 Electrolytic.

2 Volumetric : Iodide method

3 Volumetric : Cyanide method.

1 Electrolytic Assay of Copper.

The amount of ore or substance to be taken will depend on the amount of Copper which it contains.

For assays of a substance containing five per cent or less of copper three grammes should be taken, while for a substance containing over sixty per cent of Copper .25 of a gram will be sufficient. The usual amount is one gram.

Solution of copper is filtered and put into a platinium dish. This dish is best made of the lightest platnium which will adm of ordinarily careful handling when filled with solution. The platnium dish is then placed on a piece of copper or brass con nected with the negative or zinc element of battery (a very good battery for this purpose is the ordinary Bunsen cell) whi the liquid in the dish is connected with the positive pole eit by platnium wire attached to the positive pole and coiled in a horizontal spiral, or by a copper wire on which is hung a strij of platnium foil, the ends of which are immersed in the liquid. The time of assay depends on amount of copper in solution. Abo eight hours is time usually required to complete the assay.

After copper is all extracted the liquid is best removed f dish by siphoning off by means of a bent glass tube, the solu being replaced by distilled water as fast as it is siphoned of until solution is too weak to redissolve copper when current i stopped. When washed current is interrupted, water is poured of and contents dryed by setting fire to with alcohol, which adheres to sides of dish, after which the dish with its rose colored copp is weighed and copper is determined.

Another quicker way to do above is by means of using a con cathode (of platinum) and a beaker. By using the conical c you can do away with the slow work of siphoning off as the be

containing the acid solution can be removed when all the copper has been deposited.

Traces of Arsenic,Antimony and Bismuth do not interfere wi the method.

Arsenic and antimony in considerable quantity must be removed either by roasting or by wet methods. A good method of procedure when Arsenic is present is to treat ore according to method described later under the head of cyanide assay.

This method is preferable to the method described by Cairns in Cairns Quantitative Analysis, of precipitating the metals of groups six and seven by means of sulphuretted hydrogen and then dissolving sulphides of Arsenic, Antimony and Tin by the additic of Caustic Potash on account of its greater speed and the less liability of loss of copper by manipulation.

The use of sulphuretted hydrogen is not only a source of annoyance and discomfort, but without very careful manipulation, introduces a liability of error,owing to the difficulty of handl and washing the precipitate.

Taking all of the liabilities of error into consideration Messrs. Furman, Tarrey and Eaton agree that the cyanide method i generally more accurate and preferable to the battery assay. Engineering and Mining Journal, May and June 1885.

Bismuth must be separated for electrolytic assay by ammonium carbonate as described under Bismuth in Ricketts & Miller.

HNO_3 (2 - 3 cc Conc. Acid) added to the ore solution

before electrolysis will prevent the deposition of small quantities of Arsenic and Antimony. If deposition takes long nitric acid will be reduced and must be replaced.

(2) Iodide Method.

This method is the most used for accurate assays. This method is based on the fact that potassium iodide precipitates all of the copper from an acetic acid solution as $Cu_2 I_2$ liberating at the same time an equivalent quantity of iodide. The iodide is measured by sodium thiosulphate "hypo" using starch paste as indicator.

When precipitating copper on Al some of the arsenic comes down as metallic arsenic while another portion is lost as AsH_3.

After dissolving the copper and arsenic precipitate add a gram of $KClO_3$ which oxidizes the arsenic to $H_3As\ O_4$ which has no effect on I or KI and hence the Arsenic in this form does not interfere with determination.

(3) Cyanide Method.

This method is based on decolorization of an ammonical solution of Copper Nitrate by Potassium Cyanide. The reactions of the process are complicated, as different organic compounds are formed under varying conditions. For this reason it is essential to the accuracy of the method that the bulk of solution the temperature, the excess of ammonia, the quantity of ammonium salts and approximately amount of copper in solution, shall be the same as in standardizing.

In the determination of Copper from an arsenical ore by the K C N method the arsenic may be only partially precipitated by the treatment with zinc and may consequently, when the zinc is dissolved, react on the precipitated copper and casue the solutio of a small portion. With such ores more time should be allowed for the zinc to act before dissolving the excess, and also the first decantation sould be made as soon as possible after the zinc has all been dissolved.

An accurate assay by this method can be done in from twenty to thirty minutes.

(Furman's Assaying).

The titration can be done in the presence of iron, but it is not as accurate; if it is preformed in this way, standardize with a solution containing same amount of iron. Do not attempt to filter off the precipitated ferric hydrate, as it holds copper in solution which cannot be washed out.

A copper matter assayed by the three methods described gave the following results: (Furman's)

	first	second	mean
Electrolytic	53.89	53.93	53.9
Iodide	53.97	53.99	53.9
Cyanide	54.14	54.08	54.1

Dulin has introduced a method by which he can get rid of the Arsenic by boiling down to dryness several times with concentrated H Cl . This volatilizes the Arsenic as As Cl_3 . Same ca be done by means of Bromine, this volatilizes arsenic as As Br_3

Electrolytic determination of refined copper containing arsenic and antimony can be done accurately by following method: Journal American Chemical Society, Vol. 27, 1905. by Heath.

Solution of five grams arsenical copper in twenty centimeters nitric acid, add fifty centimeters of saturated solution of ammonium nitrate (NH_4NO_3)

Neutralize copper with ammonia until slightly basic then add one centimeter strong H_2SO_4 or enough to make solution slightly acid. Now fill up with ammonium nitrate solution until body of electrode is just covered. Loss from spattering can be avoided by split watch glass. Current $N.D_{100}$ .7 amperes, counting both sides of cathode as soon as the solution becomes colorless. Wash down cover and walls of beaker and reduce current to .5 amperes. $N.D_{100}$ density in amperes per square centimeter of cathode surface. Waste solution can be saved and ammonium nitrate recovered by treating neutralized solution with H_2S and evaporating to a jelly and re-solution.

DETERMINATION OF ARSENIC.

Fusion Methdd.

The determination of arsenic can be done by the following methods:

(1) The Fusion Method

(2) The distillation method.

The first is the quickest and gives very good results although the distillation method will give a more accurate result and is generally used in making umpire assays.

Fusion Method for the Determination of Arsenic.

(1) Dr. Pearce's Method.

This is a method of indirect titration based on the following facts:

Nitrate of Silver completely precipitates an alkaline arsenate in a neutral solution . As Ag_3 AsO_4 soluble in nitric acid. Silver in a nitric acid solution is completely precipitated by NH_4CNS as AgCNS

Hence for each atom of Silver found there must be one third atom of Arsenic in the ore or for 107.92 parts Silver, 25.03 parts of Arsenic.

Solutions used in the method are 1. A standard solution of Ammonium sulpho cyanide containing about eight grams of the salt per litre. In place of the above could use a solution of ten grams K C N S to a litre.
(2) A ten percent solution of ferric alum for an indicator.

To standardize the ammonium sulpho cyanide solution take about three hundred milograms of chemical pure silver foil dissolved in nitric acid. Test acid for chlorides before using as an acid containing chlorides is unfit to use. About two checks should be run.

PROCEDURE.

.5 grams ore is mixed with about six to ten times its weight of $NaCO_3$ one part and KNO_3 one part.

It is best to mix ore with about two-thirds of this flux,using the remaining third as a cover. Mixture is put in an iron crucible and heated gradually to a quiet fusion where it is kept for a few minutes.

This fusion should be done carefully at the lowest temperature possible as there is danger of a loss of arsenic from volatilization or deflagration.

A balst lamp nedd not be used as an ordinary burner will give sufficient heat.

A clear fusion cannot be obtained and the fusion can be helped greatly by the addition of a small amount of NaOH.

In determining arsenic in ores very rich in arsenic,such as arsenopyrite,nicolite,etc. it is desirable to add a few drops of fuming nitric acid to the weighed sample in a platinum crucible prior to the usual fusion.

This oxadizes the arsenic and suplher present,and prevents subsequent loss by deflagration. This precaution should also be adopted in the determination of arsenic in sulphide of arsenic obtained in the ordinary course of analysis. Allow fusion to cool and extract fusion with hot water. It is best to remove the mass by warm water,pouring into casserole,and after whole is transferred to casserole,to heat to a boiling temperature and filter.

The arsenic is in the filtrate as an alkaline arsenate,which is then acidified with nitric acid and solution boiled to expell CO_2 and

nitrous fumes. It is then cooled and almost exactly neutralized as follows:

Place a small piece of litmus paper in liquid,which should show an acid reaction and then gradually add ammonia until litmus paper turns blue,avoiding a great excess. Again make slightly acid, and then by means of very dilute ammonia and acid, added drop by drop, bring the solution to a condition that the litmus paper,after having been previously reddened,will in course of half a minute,begin to turn blue. If neutralization has caused much of a precipitate (alumina,etc.) the solution is best filtered at once in order to render the subsequent washing and filtration of the arsenate of silver more rapid. A neutral solution of nitrate of silver is now added in slight excess and color of paper is noted,and if necessary the neutralization is repeated. The second neutralization is always necessary when the amounts of arsenic are large,as nitric acid is set free in the reaction between the alkaline arsenite and silver nitrate,according to one or both of the following equations,or those of the corresponding potassium salts:

$$3\ AgNO_3 + Na_2HAsO_4 = Ag_2AsO_4 + 2NaNO_3 + HNO_3$$

The precipitated arsenate of silver,which is of a brick red color,is finally collected on a filter and well washed with cold water. Filtrate should be tested for arsenic and precipitate sould be washed until filtrate gives no test of silver. The object how is to determine the amount of silver and from this calculate the arsenic. This may be accomplished in two ways:

(1) Precipitate dryed in a scorifier,test lead and borax added, and a scorification assay made. If this method is adopted any soluable

chloride must be removed earlier in the process.

Generally but few ores will be encountered in which any soluable chloride will be present.

(2) Dissolve arsenate of silver on the filter with dilute nitric acid (which leaves undissolved any silver chloride) and titrate the filtrate,after addition of about five cubic centimeters of a saturated solution of ferric ammonium sulphate, with a standard solution of NH_4CNS. A white precipitate forms and when the end point is reached this gives a faint red tinge.

It is good to shake solution during titration as this breaks up any clots of sulphocyanate of silver,and frees any solution held mechanically.

Molybdic and phosphoric acids which behave similarly to arsenic under this treatment,interferes of course with the method.

Antimony,by forming antimonate of sodium,or potassium,remains practically insoluable and without effect. The bad point in this method is the careful neutralization which has to be done with great care as the success of the method depends upon this.

The method proposed by R.C.Cauby, Transactions of the American Institute of Mining Engineers. Vol. XVII, p 77, in which he neutralizes the solution with an emulsion of chemically pure zinc oxide does away with this. The zinc oxide is added in slight excess. No delicate testing with litmus paper and alternate adding of dilute ammonia and nitric acid becomes necessary,thus saving time. Another method for neutralization can be found in Ricketts and Miller, Notes on Assaying. The solution from the fusion- add a few drops of phenol-phthalein,then add acetic acid until decidedly acid as shown by absence of red color.

The boil off CO_2 etc. Cool and neutralize by adding Caustic soda until the indicator turns red, then add acetic acid drop by drop until color disappears.

The advantages of these methods are.

(1) The accuracy of Velthards Method for Silver which is used to determine arsenic indirectly.

(2) Since 3 ag = 1 arsenic this makes the method more accurate than before.

(3) The fusion causes a separation of almost all other substances as Iron, Copper, etc. and in this way they do not interfere in the least.

In the Pierce method the author says that the presence of antimony will not effect in the least the determination of Arsenic. This is obviously incorrect; in the fusion with sodium carbonate and potassium nitrate, the antimony if present forms salts with sodium and potassium. The salts are slightly soluble in water more so in warm water, the solubility depending upon the salt formed, some being more soluble than others. The potassium salts of antimony are more soluble than the sodium salts and therefore the error sould be lessened by the use of Na_2CO_3 and sodium nitrate in place of the potassium nitrate. The potassium salts are extremely insoluble in a solution of alcohol and water, so the error could be eliminated by the use of a solution of alcohol to put the arsenic salt into solution, thus leaving the antimony behind.

If antimony is put into solution it will form a salt of silver with the silver nitrate, which is similar in its properties to the arsenic

silver salts formed. The exact composition of this silver salt of antimony is not known but it is thought not to contain as much silver as the arsenic salt,however, even if there was a small amount of antimony put into solution it would make the determination high.

DETERMINATION OF ARSENIC DISTILLATION METHOD.

Several schemes for the determination of Arsenic have appeared of late in different chemical journals,showing that some difficulty seems to have been experienced in determining this element and that new and better methods are desired.

Pearce's method has been and is now,the one usually used in the West for smelter work.

In some cases,especially for investigation work,this is not accurate enough. Some arsenic is volatilized on making the fusion,and consequently checks are hard to arrive at in the hands of different chemists,more arsenic being lost under some conditions than in others. It has been found by Skinner and Hawley that any mixture of sulphides precipitated from an acid solution may be decomposed by a solution of cupric chloride in hydrochloric acid,and the arsenuous chloride distilled ~~and~~ very quickly. Not more than one gram of ore may be conveniently handled by the Pearce method,but with the following method any amount may be used,so that very small percentages may be determined with accuracy.

The solutions required are:

Cupric shloride:- Dissolve 300 grams pure cupric chloride crystals in one litre hydrochloric acid (sp. gr. 1.20).

This solution is mixed with one litre of a solution of zinc chloride which boils at 180 degrees C.

The zinc chloride may be made by adding successively to one pound of pure stick zinc 500 cc of water and 1250 cc of hydrochloric acid (1.2)

After the zinc is in solution bring to a boil and evaporate a little to bring the boiling point up to 180 degrees C., this making about 1100cc of solution.

Standard Iodine Solution.

This is best made so that one c.c. is equivalent to about .005 grams of arsenic. Dissolve about forty grams of potassium iodine in a minimum of water and add seventeen grams of iodine. After the iodine is all dissolved,make up to one litre with distilled water.

To standardize, dissolve three hundred milligrams of chemically pure arsenious acid (As_2O_3) in a little caustic soda or potash dilute to about 200 c.c. Acidify slightly with hydrochloric acid,add about two grams of bicarbonate of soda,some starch solution and titrate to a permanent blue. The arsenous acid contains 75.76 per cent arcenic. A check should be made by precipitating with hydrogen sulphide gas,the same amount of arsenic as that used for the standard.Filtering off the sulphide of arsenic and distilling as in a regular determination (as shown subsequently) and titrating. Deduct from all regular determinations the number of cubic centimeters required over those of the standard. This is necessary on account of the possibility of the reagents containing impurities.

It is difficult to obtain cupric chloride free from arsenic. Or, the cupric acid solution may be put into a flask with a filter paper and about two hundred milligrams of chemically pure copper,distilled and titrated,and number of c c. used deducted from the regular determinations.

The method of procedure on a gram charge,which is the amount usually taken,is as follows:

Add ten cc. of nitric acid (specific gravity 1.42) to the ore in a three inch casserole and warm. After the evolution of red fumes has nearly ceased add about ten c c. sulphuric acid (1.84 specific gravity) and run down to copious fumes of sulphuric acid. Do not boil too long after dense fumes of sulphuric acid have started or small amounts of arsenic mayn be volatilized. Allow the casserole to cool and add forty c c, cold water and ten cc. hydrochloric acid.

Some tartaric acid should be added also if antimony is to be determined.

Boil to dissolve all soluble mater. If much gangue is present, filter, if not wash in Number 3 Griffin Lipped Beaker,using warm water, and reduce to a colorless solution with a mixture of one part of ammonium bisulphide and two parts strong ammonia.

The reduction is best made by adding the ammonical sulphite solution drop by drop with constant stirring,waiting for the precipitate formed to dissolve after each addition.

Do not add any more than is necessary to reduce to colorless stage.

Add a little more hydrochloric acid in case hydrates formed do not dissolve.

If there is much gold, selenium or tellurium in the ore, these metals will be precipitated by excess sulphurous acid and darken the solution, so, if after the solution is nearly colorless this darkening occurs no more sulphide heed be added.

Boil solution a few minutes until there is no apparent oder of sulphurous acid and then while still warm pass in a lively current of hydrogen sulphide gas for about fifteen minutes, or until the precipitated particles gather together and the supernatant liquor does not appear murky.

It is safe to pass gas through a longer time, but, in case of a hurry, after some experience, the point may be told almost with certainty by inspection.

Filter precipitated sulphides through a eleven C.m. paper. Quicker to use suction filter, wash out iron salts. Test filtrate under hydrogen sulphide gas. Now put paper containing sulphides into a four ounce distillation flask, the arm of the neck of which is bent down at the end so as to connect with a twelve inch Liebig Condenser set vertically.

If the sulphides are too bulky to wrap in paper and put into flask, pierce the point of the filter and wash most of the precipitate through the funnel into the flask, using a minimum wash of one volumne hydro chloric acid (1.2) and one volumne water. Remove paper and put it into flask. Then pour through funnel to wash it fifty c c. of cupric chloride solution.

Always pour the chloride solution through a funnel reaching below the opening in side of the neck of the flask so as to avoid getting copper into the distillate.

Insert a thermometer through a rubber stopper,in the neck of the flask,reaching to within about one fourth inch of the bottom of flask. The flask is best set on a sand bath, four inches in diameter,so that the naked flask will not play on sides of flask so avoiding the raising of the temperature at any spot above that dedired. Allow outlet of the condenser to dip into about forty c,c. cold water one half an inch. It is best to keep this cool by means of water on the outside of beaker containing distillate. Heat flask gradually until thermometer reads 115° C. Then remove the stopper and add ten to twenty five cc. of strong hydrochloric acid,collecting a second distillate.

This second distillation is not necessary if the arsenic is present in small amounts. I found that in case of an ore containing about seventeen percent arsenic that more than two distillations were necessary in order to get all the arsenic off.

To be sure you have distilled off all the arsenic keep on making distillation until you find no trace of arsenic in the distillate.

The distillates are poured into a beaker made alkaline with ammonia, just acidified with hydrochloric acid,cooled,about two grams of bicarbonate of soda added, or until solution is neutralized,and some starch solution and titrate with standard iodine solution.

The use of hydrogen sulphide gas in this method seems to be the bad point about it as it brings in a great chance for error and the assayer has to be very careful in its use. When done properly very accurate results may be obtained.

A variety of ores have been run by this method and checks by different chemists show that by this method the results are about

six-tenths of a percent higher than those run by the Pearce method.

I also found the same true on a very heavy arsenic ore.

Assay by Fusion		16.96%
"	" Distillation	17.34"
"	" Diff.	.38"

Fisher Distillation Method.

This method consists of distilling of the arsenic as arsenious chloride and so affords a most perfect separation from antimony and tin.

Althoug it requires considerable apparatus,it must be regarded as the standard method of separation,Besides being applicable to ores it is even more so for material containing only very low percentages of arsenic,copper,etc.

Arsenic ores are almost always sulphides. The original ore or the sixth group sulphides,are treated as follows:

Place about two grams of potassium chlorate on the bottom of a beaker. On this place the weighed sample of ore,from .5 to three grams, depending on the richness,or the preipitated sulphides. Then about one gram more of potassium or sodium chlorate,sufficient to cover the ore. Pour in continuously,little by little, a mixture of thirty c.c. of concentrated hydrochloric acid and ten c.c. of water. Heat on a warm plate until the decomposition is complete and the oxides of chlorine, etc.driven off so as not to use up the ferrous salt used later.

It is very important that the oxidation is complete to $H_3As\ O_4$ as the arsenious chloride would be lost in boiling.

Transfer the solution to a distilling flask (about 400 c°c.) using concentrated hydrochloric acid. Add five to twenty grams of ferrous sulphate,depending upon the quantity of arsenic present and make the solution up to about 200 c.c . in volumne with concentrated hydrochloric acid. Connect flask with a short condenser and under the end place an Erlemeyer Flask about 250C.C.,containing a little water so as to cover end of condenser tube. Heat the flask on an asbestos pad. The arsenic acid is promptly reduced by the large excess of ferrous salt and forms arsenous chloride. This with hydrochloric acid beings to distill over at a temperature of 100 degrees C.

They are c ndensed and caught in the Erlemeyer flask. If this becomes very hot it should be surrounded by water.

The apparatus should be set up in a place free from draughts so as to avoid back pressure.

The distillation is continued until about half the original volumne remains. Remove the Erlemmeyer flask and then the bruner. When cool add another 100 C.C. of concentrated hydrochloric acid and repeat. Continue this until all the arsenic is distilled over.

Unless there is a very large quantity of arsenic present two or at the most three distillations are all that are required. The solution in the flask must not be allowed to become too small or in other words the boiling point must not be allowed to rise above 100 degees C. for the temperature of the vapour of 113 degrees C. for solution. Above this point antimony will distill over.

The distillation can be hastened by connecting the distilling flask with another flask containing concentrated hydrochloric acid. Into this allow concentrated sulphuric acid to drip,thus generating hydrochloric

acid gas which passes constantly through the solution, so that the strength of the acid is maintained and the removal of arsenious chloride facilitated. The distillates are treated the same as in the hydrogen sulphide gas method.

For some reasons unknown to me I have been unable to get any arsenic to distill over by the use of the above.

I have found that the arsenic was left behind by testing the solution left in the flask with Hydrogen disulphide gas.

I am going to continue work on this after the closing of school and try to obtain a satisfactory result.